CHAPTER VIII

OPTICAL STUDIES

8.1 Introduction

In the modern era of lasers and computers, the growth of thin film research and development owes much to the stimulus provided by the early utilitarian interest in the application of optical films. Thin films are widely used in optical devices such as filters, antireflection coatings and mirror coatings [1-3]. The new technology of integrated optics is based on the concept that optical circuits can be designed in analogy to the well known electronic integrated circuit [4-6]. Organic films find innumerable applications in optical devices [7-9]. Organic thin films in non-linear optics with even second order non-linearities offer the possibility of novel phenomena, devices for laser modulation and deflection and information control in optical circuitry [10]. Because of the increasing interest in thin film dye laser [11] it is instructive to consider the optical properties of organic dyes in thin film form. In all these applications, accurate knowledge of the optical properties of the films is absolutely essential.

Generally the theoretical and experimental investigations on the optical characteristics of thin films deal primarily with reflection, transmission and absorption properties and their relation to the optical constants. Moreover, the reflection and transmission properties of thin films have made it possible to evaluate the optical constants conveniently. The absorption studies have led to a variety of interesting thin film optical phenomena which have thrown considerable light on the electronic and band structure of a substance, their degeneracy, band gap energy, lattice bonding and a host of other information.
The optical properties of organic semiconducting thin films such as anthracene, tetracene and pyrene prepared by different techniques have been analysed by earlier workers [12-14]. A promising four-level fluorescing system for the creation of laser is the perylene molecule, which is photochemically stable under intensive optical irradiation [15]. p-Terphenyl is a valuable efficient lasing compound in the UV region [16]. Some work has been done earlier on the optical properties of perylene films [17]. A systematic study of the optical properties of vacuum deposited and ion plated films of perylene and p-terphenyl has been made in the present investigation.

8.2 Theory

Maxwell's electromagnetic theory relates electromagnetics and optics and attains the deduction of Maxwell's equations. From these equations it can be deduced that for a plane wave varying periodically in time with a frequency \( v = \omega / 2 \pi \) and moving in the positive x-direction with a complex propagation factor,

\[
\nu = j \omega (\epsilon \mu)^{1/2} = \alpha + j\beta
\]

where \( \alpha \) is the attenuation factor, \( \beta \) the phase factor, \( \epsilon \) the permittivity and \( \mu \) the magnetic permeability. The phase velocity of the wave is given by

\[
\nu = \frac{1}{(\epsilon \mu)^{1/2}}
\]

In vacuum, this wave travels with a phase velocity equal to that of the light (C) while it moves with a lesser velocity in any other material of the medium. The refractive index of the medium is given by the ratio of these two phase velocities as

\[
n = (\epsilon \mu)^{1/2}
\]
As the dielectric constant is a complex quantity, $\varepsilon$ has to be replaced by $\varepsilon^*$ where $\varepsilon^* = \varepsilon' - j\varepsilon''$. By similar reasoning $\mu$ can also be replaced with its respective complex term $\mu^*$. For a transparent (loss free) non-magnetic optical medium $\mu = 1$.

The equation 8.3 becomes

$$n = (\varepsilon')^{1/2} \quad \text{or} \quad n^2 = \varepsilon' \quad (8.4)$$

The absorption index (extinction coefficient) is the attenuation per unit radiation and may be written as

$$k = \frac{\alpha \lambda}{4\pi} \quad (8.5)$$

where $\alpha$ is the attenuation of the wave called the absorption coefficient and $\lambda$ the space period defining the distance traversed by the wave in a periodic time. $\alpha$, according to Lambert's law, is

$$I = I_0 \exp(-\alpha x) \quad (8.6)$$

where $x$ is the distance in the medium travelled by the wave to diminish in intensity from $I_0$ to $I$.

These equations reveal that both the dielectric constants ($\varepsilon'$ and $\varepsilon''$) and the optical constants ($n$ and $k$) are inter-related. As a consequence of equations 8.4 and 8.5, a complex refractive index is given as

$$n^* = (n + jk) \quad (8.7)$$

This is in analogy with the complex dielectric constant $\varepsilon^*$. As both $n^*$ & $\varepsilon^*$ are related by equation similar to 8.3, we have

$$\varepsilon' = n^2 - k^2 \quad (8.8)$$

and

$$\varepsilon'' = 2nk \quad (8.9)$$
where $\varepsilon'$ and $\varepsilon''$ are known as the optical dielectric constants of the material. For a non-magnetic material $n$ and $k$ are related to $\varepsilon'$ and $\tan \delta$ as

$$n = \left[ \frac{1}{2} \varepsilon' \left( \sqrt{1 + \tan^2 \delta} + 1 \right) \right]^{1/2} \quad (8.10)$$

and

$$k = \left[ \frac{\sqrt{1 + \tan^2 \delta} - 1}{\sqrt{1 + \tan^2 \delta} + 1} \right]^{1/2} \quad (8.11)$$

8.2.1 Absorption in solids

In insulators and semiconductors, the interaction of the incident electromagnetic radiation with the bound and free charges can explain the absorption and dispersion in the spectral region. The electron transitions across the forbidden gap, the interband transitions, usually occur in the ultraviolet energy region. The valence band electrons are of prime importance in the study of semiconductors and insulators. When there is no thermal energy the only possible absorption that can take place is due to the quanta of incident radiation having sufficient energy to excite the valence electrons across the forbidden zone into the empty conduction band. Because of this action, the resulting absorption spectrum is continuum of intense absorption at shorter wavelengths, bounded by more or less steep absorption edge beyond which the material is relatively transparent.

If the material under consideration is free from imperfections, it is possible to find out from the quantum mechanical basis and appropriate selection rules, the nature of electronic transition from the absorption of photon energy assuming the validity of the relations [1,18]

$$\alpha = A (h\nu - E_g)^P \quad (8.12)$$
where $A$ is a constant, $h$ the Planck's constant, $\nu$ the frequency of incident photon and $E_g$ the energy band gap. The magnitude of the exponent $P$ however determines whether transition is direct or indirect and allowed or forbidden. The optical energy gap is the minimum energy required to excite an electron from the valence band to the conduction band by an allowed optical transition [19]. For direct allowed transitions the absorption coefficient is related to the photon energy as [20-22],

$$\alpha = A (h\nu - E_g)^{1/2} \quad (8.13)$$

If the power index is 1.5, then the transition is direct but forbidden.

When the material contains defects such as impurities, dislocations, etc., then the perturbation in the system due to those defects and the interaction with phonons as quanta of the vibrational modes of lattice should be considered. These perturbations give rise to an additional transition mechanism called indirect transition which is allowed [23] only when

$$\alpha = A (h\nu - E_g)^2 \quad (8.14)$$

and forbidden if

$$\alpha = A (h\nu - E_g)^3 \quad (8.15)$$

8.3 Spectrophotometric Analysis

8.3.1 Introduction

The optical behaviour of a material is generally utilized to determine its optical constants. Films are ideal specimens for the application in reflection, transmission and interferometric studies. The transmission and reflection characteristics of the films are readily calculated from electromagnetic theory in terms of refractive index and thickness of the film. The absorption or transmission studies
in the UV-visible range offer elegant means of determining the optical band gap of a material, as the absorption in this region corresponds to electronic energy transitions in the material. The spectrophotometric analysis involves the use of a double beam spectrophotometer in the present investigation for the evaluation of optical constants of vacuum deposited and ion plated perylene and p-terphenyl thin films.

8.3.2 Theory

The optical theory of thin films has been elaborately dealt with by Heavens and Knittl [24,25]. The working hypothesis with practical bearing is based on the following assumptions. A layer is defined by two parallel dividing planes and its lateral dimensions are practically infinity. The thickness of the layer is chosen of the order of the wavelength of light. The two adjacent media are separated by a mathematical dividing plane where a discontinuous jump of refractive index occurs. For practical purposes $n$ is assumed to be dependent on the depth of the layer (called normal inhomogeneity). The factors neglected are the possible absorption and scattering of light by the polycrystalline nature of the film, roughness of substrate and interfaces, anisotropy of film material due to structure or internal stress, inhomogeneity of the film due to non stationary evaporation conditions and dispersion of optical constants of dielectric.

Harris et al. and Hass et al. [26,27] have applied the Maxwell's boundary conditions for a film on glass substrate and arrived at expressions for transmittance $(T_o)$ and reflectance $(R_o)$ at normal incidence of the incident radiation as

$$T_o = 4n_b[(n_b+1)\cos \frac{2\pi d}{\lambda} (n_f+i k_f) - i(\frac{n_b}{n_f + i k_f} + n_f + i k_f)]$$

$$\sin \frac{2\pi d}{\lambda} (n_f + i k_f) \right]^{-2}$$

(8.16)
Using the data from transmission characteristics, these two complex equations can be solved by removing the imaginary terms in the expression with the help of the corresponding modulus quantities. The subscripts 'b' and 'f' in the above equations stand for substrate and film respectively.

The absorption index \( k_f \) can be estimated either using \( T_o \) or \( T_o \) and \( R_o \) data in Lambert's equation

\[
T_o = \frac{1}{1_o} = \exp \left( - \frac{4\pi k_f d}{\lambda} \right) \tag{8.18}
\]

or

\[
T_o = (1 - R_o) \exp \left( - \frac{4\pi k_f d}{\lambda} \right) \tag{8.19}
\]

The absorption coefficient \( \alpha \) can be evaluated from the equation

\[
\alpha = \frac{4\pi k_f}{\lambda} \text{ cm}^{-1} \tag{8.20}
\]

If the films are non-absorbing i.e., the absorption is too small so that \( k_f \approx 0 \), the equations 8.16 and 8.17 can be modified accordingly [28]

\[
T_o = 4n_b \left[ (n_b + 1) \cos \frac{2\pi n_f d}{\lambda} - i \left( \frac{n_b}{n_f} + n_f \right) \sin \frac{2\pi n_f d}{\lambda} \right]^{-2}
\]
and

\[
R_o = \frac{[2\pi n_1 d}{\lambda} \cos \left( \frac{2\pi n_1 d}{\lambda} \right) + i \left( \frac{n_b}{n_f} - n_f \right) \sin \left( \frac{2\pi n_1 d}{\lambda} \right)]^2}{[2\pi n_1 d}{\lambda} \cos \left( \frac{2\pi n_1 d}{\lambda} \right) - i \left( \frac{n_b}{n_f} + n_f \right) \sin \left( \frac{2\pi n_1 d}{\lambda} \right)]^2}
\]  

(8.22)

In the case of reflection if \( m \)th order maximum occurs at \( \lambda_1 \) and \((m+1)\)th order at \( \lambda_2 \), the expression for normal incidence (considering the same refractive index for \( \lambda_1 \) and \( \lambda_2 \)) can be given by [29]

\[
2n_1 d = m\lambda_1 = (m+1)\lambda_2
\]  

(8.23)

or

\[
n_1 = \frac{\lambda_1 \lambda_2}{2d(\lambda_1 - \lambda_2)}
\]  

(8.24)

This method may be used to determine the refractive index of films since the refractive index does not vary rapidly with the wavelength.

8.3.3 Experimental

The optical transmission measurements were made in the UV and visible regions at near normal incidence for all the film samples deposited on glass substrates. In the investigation, JASCO-UV/VISIBLE spectrophotometer (Model UV/DEC-610, Japan) with heat sensitive graphic printing recorder fed with heat sensitive chart paper (J-0063), was used (Figure 8.1). It is also provided with CRT (Cathode Ray Tube) monitor having graphic display at high resolution. The spectrophotometer has a wavelength range of 195 to 900 nm with an accuracy of ± 0.3 nm. Transmission spectra were recorded for the samples.
FIG. 8-1 JASCO SPECTROPHOTOMETER
The optical constants have been evaluated from the measured values of the transmittance, the wavelength of light, the film thickness and the refractive index of the substrate using the relation

\[
\frac{4n_b}{T_0} = \left[ (n_b+1) \cos \frac{2\pi d}{\lambda} (n_f+ik_f) - i\left( \frac{n_b}{n_f + ik_f} + n_f + ik_f \right) \sin \frac{2\pi d}{\lambda} (n_f+ik_f) \right]^2
\]

and following the iterative procedure.

8.3.4 Results and discussion

Transmission characteristics of perylene and p-terphenyl films of various thicknesses, prepared by different techniques have been given in Figures 8.2 and 8.3 respectively. It is clear from the figures that the transmittance in the visible region is fairly high and increasing slowly with the wavelength. At higher wavelength region it tends to become constant. This suggests that the films are non-absorbing at higher wavelength region. The non-absorbing nature of the organic films has already been established by Olen Engelsen [30].

It has been observed from the Figures 8.2 and 8.3 that the ion plated films are more transparent than the vacuum deposited films, irrespective of the material. It could be explained on the fact that the increased density [31] caused by reduced imperfections of ion plated films may decrease the internal scattering of light.

Table 8.1 presents a comparative spectral data of perylene films and crystal. A careful examination of the table indicates that the principal features of the film perceived in the earlier work [17] are fairly in agreement with those vacuum deposited film in the present investigation. A sharp band observed at 3400 Å in the spectrum [Figure 8.2 (i)] of the present study may not have a comparison with the earlier
FIG. 8.2 TRANSMISSION SPECTRA OF PERYLENE FILMS (i) VACUUM DEPOSITED FILMS (ii) ION PLATED FILMS
FIG. 8.3  TRANSMISSION SPECTRA OF p-TERPHENYL FILMS
(i) VACUUM DEPOSITED FILMS
(ii) ION PLATED FILMS
Table 8.1
Optical spectral data for perylene films and crystal

<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>Nature of the sample</th>
<th>Data mode</th>
<th>Positions of characteristic bands in the spectra</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Vacuum deposited film</td>
<td>Absorption</td>
<td>Broad peak at ~5000 Å, 4000 Å, 3800 Å, 3400 Å, 3700 Å</td>
<td>[17]</td>
</tr>
<tr>
<td>2.</td>
<td>Crystal</td>
<td></td>
<td>4100 Å peak, 4500 Å peak, 3700 Å peak</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Absorption II a-axis</td>
<td>Absorption</td>
<td>No structure</td>
<td>[33]</td>
</tr>
<tr>
<td></td>
<td>Absorption II b-axis</td>
<td>Absorption</td>
<td>No structure</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>Vacuum deposited film</td>
<td>Transmission</td>
<td>4700 Å weak peak, 4100 Å broad peak, 3800 Å sharp peak</td>
<td>Present study</td>
</tr>
<tr>
<td>4.</td>
<td>Ion plated film</td>
<td>Transmission</td>
<td>No structure</td>
<td>Present study</td>
</tr>
</tbody>
</table>

No 3700 Å Structure
4100 Å - 3750 Å
4500 Å
4700 Å
4400 Å peak
work since the absorption spectrum obtained in that work was only in the range of wavelength 3500 - 7000 Å. Moreover, the peaks at 3400 Å, 3800 Å and 4700 Å noticed in the spectrum of vacuum deposited, crystalline film are absent in that [Figure 8.2(ii)] of ion plated amorphous film. In this connection mention may be made about the absence of peaks at 5380 Å [32] and 3500 Å [34] in the case of amorphous film of violanthrene-A, observed by earlier investigators which is similar to the present observation. In the earlier studies [34,35] on perylene films, the absorption spectrum of crystalline film was found to give rise to extra peaks at the same positions as in the present case which are also absent in amorphous films. The disordered structure is very unfavourable for the Charge Transfer (CT) transition [34]. The absorption band at 3800 Å is assigned to the CT band for perylene [36]. In the disordered perylene film formed by ion plating technique in the present work, the CT band is found to disappear. Hence, it is surmised that the appearance of additional characteristic bands observed in the transmission spectrum of vacuum deposited perylene film in the present investigation may be due to its crystalline nature.

The absorption indices (kₐ) and the refractive indices (nₐ) were evaluated in the wavelength range 4000-7000 Å, as discussed earlier in the experimental section of this chapter and their dependences on wavelength of the incident radiation and the thickness of the film were shown in Figures 8.4 to 8.7. It has been observed that in general, the absorption indices increase with increase of incident photon energy and decrease with increase of film thickness in these films. This behaviour may be attributed to the presence of voids and discontinuities in thinner films. Similar observation has been made by earlier workers [14]. In the case of ion plated films, the absorption indices are comparatively lower than those of vacuum deposited films, which may be due to lower degree of internal voids and discontinuities in the
FIG. 8.4 DEPENDENCE OF ABSORPTION INDICES ($k_f$) AND REFRACTIVE INDICES ($n_f$) OF VACUUM DEPOSITED PERYLENE FILMS
FIG. 8.5 DEPENDENCE OF ABSORPTION INDICES ($k_f$) AND REFRACTIVE INDICES ($n_f$) OF ION PLATED PERYLENE FILMS
FIG. 8-6 DEPENDENCE OF ABSORPTION INDICES ($k_f$) AND REFRACTIVE INDICES ($n_f$) OF VACUUM DEPOSITED P-TerpHENYL FILMS
Dependence of absorption indices ($k_f$) and refractive indices ($n_f$) of ion plated p-terphenyl films.
ion plated films, caused by rise in surface temperature, enhancing diffusion in the surface region due to a flux of high energy ions [31]. With respect to the dependence of refractive index on wavelength and thickness of all the films, no consistent trend is observed.

It is an established fact that the highly transparent films will have their absorption edge in the UV region [37]. This is in conformity with the present observation (Figures 8.2 and 8.3) made with perylene and p-terphenyl films deposited by both the techniques. The absorption coefficient $\alpha$ can be obtained from the transmission curves. For direct allowed transitions, the absorption coefficient and photon energy are related by the expression [38]

$$\alpha \text{(direct)} = A (h \nu - E_g)^{1/2}$$

where $A$ is a constant and $E_g$ the direct energy gap. Graphs plotted between $\alpha^2$ and $h \nu$ (Figures 8.8 to 8.11) have been found to be linear in accordance with the theoretical expectation, from which the energy gap has been estimated for each film sample. Table 8.2 presents the band gap energies obtained for different film specimens. From the table, one can find the difference in the band gap energies of the same film material but prepared by different techniques. The use of suitable deposition techniques makes it possible to obtain a material in thin film form with different micro-structures. Any change in electronic structure of the material would be reflected in the optical behaviour [39]. Therefore, the change in the optical band gap energy of vacuum deposited and ion plated films of same material may be ascribed to variation in the deposition technique.
FIG. 8-8 VARIATION OF $a^2$ WITH INCIDENT PHOTON ENERGY ($h\nu$) FOR VACUUM DEPOSITED PERYLENE FILM ($t = 2040 \text{ Å}$)
FIG. 8.9 VARIATION OF $\alpha^2\times10^{-8}$ WITH INCIDENT PHOTON ENERGY ($h\nu$) FOR ION PLATED PERYLENE FILM ($t = 2100 \ \text{Å}$)
FIG. 8.10 VARIATION OF $\alpha^2$ WITH INCIDENT PHOTON ENERGY ($h\nu$) FOR VACUUM DEPOSITED p-TERPHENYL FILM ($t = 2400$ Å)
FIG. 8-11 VARIATION OF $\alpha^2$ WITH INCIDENT PHOTON ENERGY ($h\nu$) FOR ION PLATED p-TERPHENYL FILM ($t = 1950$ Å)
<table>
<thead>
<tr>
<th>Film material</th>
<th>Deposition technique</th>
<th>Optical band gap energy, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perylene</td>
<td>Vacuum deposition</td>
<td>2.36</td>
</tr>
<tr>
<td></td>
<td>Ion plating</td>
<td>2.44</td>
</tr>
<tr>
<td></td>
<td>Vacuum deposition</td>
<td>1.56</td>
</tr>
<tr>
<td>p-Terphenyl</td>
<td>Ion plating</td>
<td>1.94</td>
</tr>
</tbody>
</table>
8.4 Modified Abele's Technique

8.4.1 Introduction

Abele's technique, which involves the measurement of Brewster's angle, can be used for the determination of the refractive index of homogeneous isotropic films on transparent substrates, with least complication yet moderate accuracy \([40,41]\). This method of measurement is limited to films whose index of refraction is within ± 0.3 of that of the substrate \([40]\). Hacskaylo \([42]\) has modified this Brewster angle technique and further extended where the refractive index of the film need not necessarily be close to that of the substrate. The refractive indices of Langmuir films of barium margarate and behanate have been found by Tomar and Srivastava \([43]\) using a similar method. Owing to the simplicity and high degree of accuracy of modified Abele's technique, it has been employed here for the estimation of refractive indices of films prepared in the present work.

8.4.2 Theory

8.4.2.1 Bulk dielectrics

The Brewster angle of the film is the angle of incidence where the intensities of reflection from the film and the substrate match when the incident light is plane-polarised and parallel to the plane of incidence and the reflected light is viewed through an analyser that is also parallel to the plane of incidence. Modified Abele's technique incorporates incident plane-polarised light with the direction of vibration nearly parallel to the plane of incidence.

When plane-polarised light is reflected from a bulk dielectric (glass), the reflected light will also be plane polarised. If the incident light is composed of components that are parallel (P component) and perpendicular (S component) to the plane
of incidence, the direction of vibration of reflected light will be rotated through some angle with respect to the direction of vibration of the incident light. At the Brewster angle, the direction of vibration of the reflected light will be perpendicular to the plane of incidence, i.e., all the P components will be transmitted. The angular change in the rotation of the reflected light could be enhanced near the Brewster angle by allowing the incident S components to be small compared to the P components [44]. This condition can be obtained, if the direction of vibration of the incident light is within a few degrees of the plane of incidence.

Fresnel's laws of reflection, based on electromagnetic theory, describe the behaviour of reflected light at the boundary of two optically different media. The rotation of plane-polarised light reflected from dielectric surface is expressed as [45]

\[
\tan \psi_r = \left[ -\frac{\cos (\phi_o + \phi_3)}{\cos (\phi_o - \phi_3)} \right] \tan \psi_i \tag{8.25}
\]

where \( \psi_r \) is the azimuth of vibration of the reflected light, \( \phi_o \) the angle of incidence, \( \phi_3 \) the angle of refraction and \( \psi_i \) the azimuth of the incidence light (Figure 8.12). At the Brewster angle, the reflected P components will be zero and the angle \( \psi_r \) will be zero. So, the reflected component will be parallel to the S direction. Then the Brewster angle is defined as the angle of incidence for which the reflected and refracted rays are perpendicular to each other, i.e., \( \phi_o + \phi_3 = \pi /2 \). The angle \( \phi_o \) is designated as \( \phi_B \) at the principal angle of incidence. At \( \phi_B \), when \( \phi_o + \phi_3 = \pi /2 \), it can be seen from equation 8.25 that

\[
\tan \psi_r = 0
\]

and consequently, the angle \( \psi_r = 0 \).
FIG. 8.12 VECTORIAL REPRESENTATION OF (a) THE REFLECTED AND REFRACTED LIGHT AT THE SURFACE OF A SUBSTRATE AND (b) THE INCIDENT AND REFLECTED AZIMUTHS OF PLANE-POLARISED LIGHT WITH RESPECT TO THE 'S' AND 'P' COMPONENTS (AXES), THE ANALYSER ANGLE IS ALSO NOTATED.

FIG. 8.13 VECTORIAL REPRESENTATION OF THE REFLECTED AND REFRACTED LIGHT AT THE SURFACE (S) OF A FILM COATED SUBSTRATE.

FIG. 8.14 VECTORIAL REPRESENTATION OF THE INCIDENT AND REFLECTED AZIMUTHS OF POLARISED LIGHT AFTER THE REFLECTION OF PLANE POLARISED LIGHT FROM A FILM COATED SUBSTRATE, THE ANALYSER ANGLE IS ALSO NOTATED.
The principal angle of incidence $\Phi_B$ can be determined by measuring the angle where the azimuth of the reflected light $\Psi_r$ is zero. The azimuth of reflection $\Psi_r$ of the reflected light can be measured by placing an analyser in the path of the reflected beam. The intensity $I_R$, of the plane polarised light reflected from the substrate and transmitted by the analyser is

$$I_R = I_{OR} \cos^2 \alpha_r$$

where $R_p$ is the reflected amplitude parallel to the plane of incidence, $R_s$ the reflected amplitude perpendicular to the plane of incidence and $\alpha_r$ the angle between the plane of vibration of the reflected light and the plane of the analyser. The angle between the analyser and the plane of incidence is defined as $\Theta$. The angles $\alpha_r$, $\Theta$, $\Psi_r$ and $\Psi_i$ are shown in Figure 8.12 (b) and can be seen that $\alpha_r = (\pi/2) - (\Psi_r + \Theta)$. At any angle of incidence, the intensity, $I_R$ will be zero when the plane of analyser angle is normal to the reflected (and rotated) plane-polarised light. If the analyser angle is zero when the plane of analyser is parallel to the plane of incidence, there will be an angle $\Theta$ where $I_R$ will be minimum (zero) and thus the angle $\alpha_r = \pi/2$. At the Brewster angle $\Phi_B$, not only $I_R$ is zero but also $\Psi_r$ must be zero. Since $\alpha_r = \pi/2$, $\Theta$ must be zero. Thus under these conditions, the Brewster angle can be determined when the analyser angle is zero. The refractive index of glass substrate $n_2$ [Figure 8.12 (a)] can be given by the Brewster law

$$n_2 = n_o \tan \Phi_B$$

where $n_o$ is the refractive index of air and $\Phi_B$ the principal angle of incidence for the substrate.
8.4.2.2 Thin film on a transparent substrate

The optical properties of a dielectric film on a glass substrate can be expressed in terms of the Fresnel coefficients for the reflection and transmission of the light vibrating parallel and perpendicular to the plane of incidence for each boundary of the optical system. With reference to Figure 8.13, the reflection coefficients can be expressed as

\[
\begin{align*}
    r_{1p} &= \frac{(n_0 \cos \phi - n_1 \cos \phi_0)}{(n_0 \cos \phi_1 + n_1 \cos \phi_0)} \\
    r_{2p} &= \frac{(n_1 \cos \phi_2 - n_2 \cos \phi_1)}{(n_1 \cos \phi_2 + n_2 \cos \phi_1)} \\
    r_{1s} &= \frac{(n_0 \cos \phi - n_1 \cos \phi_0)}{(n_0 \cos \phi_0 + n_1 \cos \phi_1)} \\
    r_{2s} &= \frac{(n_1 \cos \phi_1 - n_2 \cos \phi_2)}{(n_1 \cos \phi_1 + n_2 \cos \phi_2)}
\end{align*}
\]

The subscripts 1 and 2 denote the boundaries between \( n_0, n_1 \) and \( n_1, n_2 \) media. The amplitudes for reflection of a film-coated substrate expressed in terms of the reflection coefficients are given as

\[
\begin{align*}
    R_p &= r_p e^{i\delta} = \frac{(r_{1p} + r_{2p} e^{-2i\delta})}{(1 + r_{1p} r_{2p} e^{-2i\delta})} \\
    R_s &= r_s e^{i\delta} = \frac{(r_{1s} + r_{2s} e^{-2i\delta})}{(1 + r_{1s} r_{2s} e^{-2i\delta})}
\end{align*}
\]
\[ \delta_1 = \left[ \frac{2\pi n d}{\lambda} \right] \cos \Phi_1 \]  
where \( \delta_1 \) is the thickness of the film, \( \Phi_1 \) the angle of refraction, \( d \) is the thickness of the film, \( \lambda \) the wavelength of light. Due to the finite thickness of the film a change in phase occurs between the \( P \) components and \( S \) components. The reflected elliptically polarised light can be treated as linearly polarised light \([46]\). In this approximation, the azimuth of the reflected light would also be the angular direction of the major axis of the narrow ellipse as measured from the \( S \) direction. This angle is shown as \( \Psi_r \) in Figure 8.14. The azimuth of the reflected light from the substrate would be at some angle \( \Psi_r \) which is also shown in the same figure.

The intensity \( I'_R \) of the light reflected from the film coated substrate and transmitted by the analyser is

\[ I'_R = I''_{OR} \cos^2 \alpha'_r \]  
(8.35)

Let

\[ I''_{OR} = (R'_p^2 + R'_s^2) \]  
(8.36)

where \( R'_p \) and \( R'_s \) are the reflected amplitudes of the film coated substrate and \( \alpha'_r \) is the angle between the plane of vibration of the reflected light from the film coated substrate and the plane of the analyser.

The vectorial representation of equations 8.26 and 8.35 and the solutions for \( \Theta_M \) are shown in Figures 8.15(a), (b) and (c). For a given angle of incidence \( \Phi_o \), the azimuth of the reflected light from the substrate is \( \Psi_r \), and the azimuth of the reflected light from the film coated substrate is \( \Psi'_r \). \( OA \) is the direction parallel to the plane of incidence and \( OB \) that of vibration of the linearly polarised light reflected from the substrate. \( OC \) is the direction of the major axis of the elliptically polarised light reflected from the film coated substrate. The direction of vibration is arbitrarily projected along \( OB \) and \( OC \) for \( I_{OR} \) and \( I''_{OR} \) respectively. The angle \( \Theta_M \) is the analyser angle where the reflected intensity \( OM \) is common to the substrate and film coated substrate (as seen through the analyser).
FIG. 8.15 GRAPHIC REPRESENTATION OF THREE GENERAL SOLUTIONS SHOWING THAT THE INTENSITIES OF REFLECTED LIGHT FROM A SUBSTRATE AND FILM-COATED SUBSTRATE MATCH AT SOME ANALYSER ANGLE FOR AN ANGLE OF INCIDENCE OTHER THAN THE BREWSTER ANGLE FOR THE FILM OR SUBSTRATE
Depending upon the intensities of the reflected light from the system, there arise three general cases:

i) when the reflected intensity of the substrate is equal in the magnitude to that \( (I'(OR)) \) reflected from the film coated substrate, the reflected intensities match at an angle \( \theta_M \) along OM [Figure 8.15(a)], ii) when the reflected intensity of the film coated substrate is less in magnitude than that reflected from the substrate, the analyser angle of matching intensities is then at some \( \theta_M \) along OM [Figure 8.15(b)] and iii) when the reflected intensity of the film coated substrate is greater in magnitude than that reflected from the substrate, the angle of the matching condition will be at some other angle \( \theta_M \) along OM [Figure 8.15(c)].

Abele's conditions are satisfied if the reflected intensities of the P component light from the substrate surface and the film coated substrate match the principal angle of incidence \( \phi_B \) of the film. For the existence of this condition, the amplitude of the reflected P component light from the film surface is zero, but the amplitude of reflected P component light from the film-substrate interface and the substrate are not zero. This is due to the fact that the principal angles of incidence for the film and the substrate are not the same. As the direction of the allowed vibration of the analyser is parallel to the plane of the incidence, any S component of the reflected light will be absorbed by the analyser. Therefore, at the Brewster angle of the film, \( \theta_M \) is zero and the Abele's conditions are satisfied. Thus if the angle of incidence \( \phi_o \) satisfying the Abele's condition is known, the refractive index \( n_1 \) of the film can be found by the use of the simple relation \[40,47\],

\[
\begin{align*}
    n_1 &= n_o \tan \phi_B
\end{align*}
\]  

(8.37)

where \( n_o \) is the refractive index of air.
8.4.3 Experimental

Thin films of perylene and p-terphenyl were formed on glass substrates by vacuum evaporation and ion plating techniques as described in Chapter III. The refractive indices of those films were evaluated using Hacskaylo's modified Abele's technique. The schematic diagram of the Abele's set up and the actual experimental arrangement are illustrated in Figures 8.16 and 8.17 respectively. The arrangement consists of a monochromatic light source (\( \lambda = 5893 \text{ Å} \)), a condensing lens and a research spectrometer with polariser and analyser mounted in front of the collimator and telescope respectively. The spectrometer is with a least count of 20" while the polariser and analyser have an accuracy of 1' each. As discussed earlier in the theory, the polarised light from the polariser with the plane of polarisation nearly parallel to the plane of incidence, falls on the film/substrate. The reflected light passed through the analyser and the analyser angle for which the reflected light from the uncoated substrate and from the film coated substrate are equal has been measured. These analyser angles are plotted against the angle of incidence and the Brewster angle \( \Phi_B \) has been obtained.

The intensity for minimum reflections was sensed by a photomultiplier tube (IP21) energised with a d.c. power supply. Precautions have been taken to reduce the dark current to a minimum value. The measurement of the angle of incidence \( \Phi_o \) does not depend on the accuracy of the analyser at the Brewster angle. The steepness of the curve depends on the azimuth of the incident light. The reliability has been verified by measuring the refractive index of glass slide.

8.4.4 Results and discussion

The analyser angle \( \Theta \) has been plotted as a function of the angle of incidence \( \Phi_o \) for glass slides as depicted in Figure 8.18. The mean of the Brewster angle for glass substrate has been found to be 56° 30' and the refractive index calculated from
FIG. 8.16 SCHEMATIC REPRESENTATION OF THE EXPERIMENTAL ARRANGEMENT OF MODIFIED ABELE'S (HACSAYLO'S) METHOD

1. LIGHT SOURCE
2. CONDENSING LENS
3. COLLIMATOR
4. POLARIZER
5. ROTATABLE STAGE
6. SPECIMEN HOLDER
7. ANALYZER
8. TELESCOPE
9. PHOTOMULTIPLIER HOUSING
10. PHOTOMULTIPLIER TUBE (IP21)
11. D.C. POWER SUPPLY
12. NANOAMMETER
FIG 8.17 EXPERIMENTAL SETUP OF MODIFIED ABELE'S TECHNIQUE
FIG. 8.18  ANALYSER ANGLE FOR MINIMUM INTENSITY OF PLANE POLARISED LIGHT REFLECTED FROM GLASS SUBSTRATE AS A FUNCTION OF ANGLE OF INCIDENCE
the equation 8.28 is 1.51. This is in close agreement with the reported value of refractive index for glass slides [42,48].

Figures 8.19 to 8.22 display the plots of analyser angle ($\Theta_M$) for matched film substrate reflections as a function of angle of incidence for the films of perylene and p-terphenyl formed by the different deposition methods. The refractive indices of the films estimated by spectrophotometric and modified Abele's techniques for different thicknesses are presented in Table 8.3. An examination of the table reveals that there is a fair agreement between the values of refractive indices obtained by both the methods.
FIG. 8.19 ANALYSER ANGLE FOR MATCHED INTENSITIES OF PLANE POLARISED LIGHT FROM UNCOATED AND VACUUM DEPOSITED PERYLENE FILM COATED SUBSTRATES AS A FUNCTION OF THE ANGLE OF INCIDENCE
FIG. 8.20 ANALYSER ANGLE FOR MATCHED INTENSITIES OF PLANE POLARISED LIGHT FROM UNCOATED AND ION PLATED PERYLENE FILM COATED SUBSTRATES AS A FUNCTION OF THE ANGLE OF INCIDENCE
Fig. 8.21  Analyser angle for matched intensities of plane polarised light from uncoated and vacuum deposited p-terphenyl film coated substrates as a function of the angle of incidence.
FIG. 8.22 ANALYSER ANGLE FOR MATCHED INTENSITIES OF PLANE POLARISED LIGHT FROM UNCOATED AND ION PLATED p-TERPHENYL FILM COATED SUBSTRATES AS A FUNCTION OF THE ANGLE OF INCIDENCE
Table 8.3
Comparison of refractive indices determined by Abele's and Spectrophotometric methods

<table>
<thead>
<tr>
<th>Film material</th>
<th>Preparation process</th>
<th>Thickness Å</th>
<th>Abele's technique $n_f$</th>
<th>Spectrophotometric method $n_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perylene</td>
<td>Vacuum evaporation</td>
<td>750</td>
<td>1.208</td>
<td>1.210</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2040</td>
<td>1.204</td>
<td>1.204</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5360</td>
<td>1.317</td>
<td>1.324</td>
</tr>
<tr>
<td></td>
<td>Ion plating</td>
<td>810</td>
<td>1.217</td>
<td>1.220</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1350</td>
<td>1.224</td>
<td>1.221</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2100</td>
<td>1.205</td>
<td>1.204</td>
</tr>
<tr>
<td>p-Terphenyl</td>
<td>Vacuum evaporation</td>
<td>660</td>
<td>1.303</td>
<td>1.301</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2400</td>
<td>1.204</td>
<td>1.201</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5000</td>
<td>1.402</td>
<td>1.404</td>
</tr>
<tr>
<td></td>
<td>Ion plating</td>
<td>550</td>
<td>1.192</td>
<td>1.200</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1950</td>
<td>1.213</td>
<td>1.204</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3000</td>
<td>1.327</td>
<td>1.322</td>
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References


